

PATENT SPECIFICATION

(11) 1 255 797

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NO DRAWINGS

- (21) Application No. 59100/68 (22) Filed 12 Dec. 1968
 (31) Convention Application No. 79413 (32) Filed 12 Dec. 1967 in
 (33) Japan (JA)
 (45) Complete Specification published 1 Dec. 1971
 (51) International Classification C 08 f 25/00, 1/00
 (52) Index at acceptance C3G 1B2 1C2 2B 2C 3A2 3C4



(54) METHOD FOR PRODUCING A HEAT RESISTANT GRAFT COPOLYMER

(71) We, JAPAN SYNTHETIC RUBBER Co., LTD., a Company organised and existing under the laws of Japan of 1, 1-chome, Kyobashi, Chuo-ku, Tokyo, Japan do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a method of preparing a heat resistant graft copolymer of good processability.

15 It is known that thermoplastic resins formed by the graft copolymerization of a rubber-like polymer such as polybutadiene rubber, styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR) and the like with styrene or the mixture of styrene and acrylonitrile, which are called high impact polystyrene or ABS resin, respectively, have excellent processability and high impact strength, and are preferably used for injection moulding.

20 However, these thermoplastic resins have disadvantageously low heat distortion temperatures (lower than 90°C according to the test of ASTM D—648—56) and low heat resistance properties such as high heat shrinkage. Therefore, the graft copolymerized thermoplastic resins are not applicable in a field where high heat resistance is required, for example, car parts.

35 It has been proposed to use α -methylstyrene in place of styrene in order to improve the heat resistance property of such thermoplastic resins as mentioned above.

40 For example, the Japanese Patent Publication No. 697/1962 discloses that the copolymerization of α -methylstyrene with methyl methacrylate in the presence of an elastomer results in the formation of thermoplastic resin having a heat distortion temperature ranging from 97 to 116.5°C.

Further, U.S. Patent Specification No. 2,908,661 discloses a resin having a heat dis-

tortion temperature of at least 98°C obtained by graft copolymerizing polybutadiene, α -methylstyrene and acrylonitrile.

These resins have improved heat resistant properties, but are inferior in such properties as processability, mechanical strength and surface gloss.

Now the inventors, as a result of their researches to overcome the above given drawbacks, have found that thermoplastic resins having high heat resistant property and well balanced overall properties such as processability, mechanical strength, surface gloss, and the like can be obtained by graft copolymerization of a mixture of vinyl monomers including α -methylstyrene on to a rubber-like polymer in latex state in which a part of the monomer mixture is first graft-copolymerized by using an oil-soluble organic peroxide as initiator and then the remaining monomers are graft-copolymerized by using a water soluble persulphate as initiator. (This discovery is the subject of British Patent Application No. 37486/68, Serial No. 1,233,428.

A satisfactory result, to some extent, is obtained when the heat resistant graft copolymer obtained in accordance with the method of the above cited patent application is used in applications which require excellent heat resistance, for example, car parts.

75 However, along with the development of the plastics industry, the improvement of productivity, complicated and larger products have been recently in increasing demand, and in order to satisfy this demand, it is necessary to improve the processability of the shaped articles.

85 For this purpose, counter-measures such as improvements in shaping machines, or shaping conditions have been taken, but these counter-measures can only alter conditions to a limited extent, and it is not possible to satisfy all the physical properties (for example, mechanical strength, surface lustre, and colour), and it

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is not always possible to produce shaped articles of high commercial value.

It is one of the important problems at present to improve the processability of resins to be used, and there is a tendency for a demand for better heat resistance since the kinds and forms of the shaped articles in fields where heat resistance is required, are diversifying.

The inventors have found it possible to produce a graft copolymer having improved processability and heat resistance and well balanced properties such as mechanical strength and surface gloss when compared with those obtained in accordance with the conventional processes, and the inventors have arrived at this invention on the basis of the above described discovery.

According to the invention, there is provided a method of preparing a heat resistant graft copolymer of improved processability which comprises graft copolymerizing from 70 to 95 parts by weight of a vinyl monomer mixture containing 15 to 45% by weight of methyl methacrylate and from 20 to 65% by weight of α -methylstyrene with from 5 to 30 parts by weight of a synthetic rubber in latex state, wherein from 25 to 50% by weight of the vinyl monomer mixture containing from 40 to 80% by weight of methyl methacrylate and from 0 to 15% by weight of α -methylstyrene is graft copolymerized in the presence of an oil soluble organic peroxide initiator, and then the remaining vinyl monomer mixture is graft copolymerized in the presence of a water-soluble persulphate initiator.

The term "vinyl monomer" as used herein includes vinylidene monomers.

Thus, in accordance with this invention it is possible to obtain thermoplastic resins of high heat distortion temperature, having improved processability and thermal shrinkage when compared with the thermoplastic resins obtained in accordance with conventional methods, and having better mechanical strength and surface gloss.

Preferably the synthetic rubber comprises polybutadiene, styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR) and like butadiene rubbers.

In particular, polybutadiene and SBR are especially preferable. A mixture of polybutadiene and SBR is also preferably used.

On the other hand, butadiene rubbers containing carboxylic acid radicals obtained by copolymerizing a small amount of maleic acid, acrylic acid, or itaconic acid can also be used with advantage.

As vinyl monomers to be graft copolymerized in accordance with this invention, methyl methacrylate and α -methylstyrene as the indispensable components together with vinyl aromatic compounds (other than α -methylstyrene) and/or vinyl cyanides can be used.

As examples of vinyl aromatic compounds other than α -methylstyrene, styrene and vinyl toluene are preferable, and in particular, styrene is preferable.

As the examples of vinyl cyanides, acrylonitrile and methacrylonitrile are preferable and acrylonitrile is particularly preferable.

The following are the preferable combinations of vinyl monomers to be graft copolymerized:

methyl methacrylate: α -methylstyrene: styrene
methyl methacrylate: α -methylstyrene: acrylonitrile
methyl methacrylate: α -methylstyrene: styrene: acrylonitrile.

The last one, i.e. a combination of four components, is especially preferable.

The ratio of synthetic rubber to vinyl monomer should be 5:95—30:70.

When the synthetic rubber is less than the relative minimum, the impact strength is lowered, and when it is over the relative maximum, the hardness and heat distortion temperature deteriorate.

In order to produce a resin having well balanced properties such as mechanical strength or surface gloss, more excellent processability and heat resistance when compared with the resins obtained in accordance with conventional methods, the content of methyl methacrylate and α -methylstyrene contained in the vinyl monomer mixture to be graft copolymerized should be from 15 to 45% by weight and 20 to 65% by weight, respectively, based on the amount of the combined monomers, and the vinyl monomer mixture is graft copolymerized in two steps by dividing the total amount into two, and the amount of vinyl monomer mixture used in the first step should be within the range from 25 to 50% by weight based on the amount of the whole mixture and the amount of methyl methacrylate should be within the range from 40 to 80% by weight and the amount of α -methylstyrene should be not greater than 15% by weight.

In the first step, α -methyl styrene may be totally excluded. When the ratio of the monomer is outside the above specified range, it is not possible to obtain the effect of the present invention, as is shown in the Reference examples given below.

The most important characteristic of this invention resides in that as the vinyl monomer to be graft copolymerized to a synthetic rubber latex, the monomer mixture containing methyl methacrylate and α -methyl styrene is used as an indispensable component, and the first step graft polymerization, in which at least part of the methyl methacrylate is polymerised is carried out by using an oil soluble organic peroxide as the initiator, and the second step graft copolymerization is carried out by using

a water soluble persulphate as the initiator.

When processes other than those described above are used, it is not possible to attain the object of this invention.

- 5 Organic peroxides and persulphates which are used as the initiators in this invention are known to those skilled in the art, but examples of organic peroxides include benzoyl peroxide, and hydroperoxides such as cumene hydroperoxide, diisopropylbenzene hydroperoxide, and paramenthane hydroperoxide. More than one initiator may be used.

- 10 Particularly, redox formulations such as sugar containing pyrophosphate formulations, non-sugar containing pyrophosphate formulations, peroxamine formulations and, sulfoxylate formulations, containing a hydroperoxide, are preferable.

- 15 As persulphates, potassium persulphate and/or ammonium persulphate are particularly preferable.

- 20 Graft copolymerization itself is well known to those skilled in the art. The vinyl monomers graft copolymerized in two steps may be added in each step either at once or continuously as the reaction proceeds.

The following examples are given as illustrative of the invention.

- 25 In the examples, parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

- Polymerization was carried out in such a manner that 22 parts by weight of methyl methacrylate, 11 parts by weight of styrene, 35 3 parts by weight of acrylonitrile, 1.0 part by weight of tertiary dodecyl mercaptan, 1.0 part by weight of disproportionated potassium rosinate, and 150 parts by weight of water were added to 15 parts by weight (solids context) of polybutadiene latex, and the initiator consisting of 0.42 part by weight of cumene hydroperoxide, 0.7 part by weight of dextrose, 0.5 part by weight of sodium pyrophosphate and 0.01 part by weight of ferrous sulphate was added thereto and the reaction proceeded at 70°C for two hours with stirring.

The conversion was 96%.

- 37 parts by weight of α -methylstyrene, 12 parts by weight of acrylonitrile, 1.0 part by weight of disproportionated potassium rosinate, 0.2 part by weight of tertiary dodecyl mercaptan, 100 parts by weight of water, and 0.2 part by weight of potassium persulphate were then added to the reaction mixture at once, and the reaction mixture was stirred at 60°C for four hours. The graft copolymer latex was obtained at a conversion of 96%.

- The quantitative relation between polybutadiene and vinyl monomer mixture in the said graft copolymerization was as follows: 15 parts of polybutadiene and 85 parts of vinyl monomer mixture containing 26% of methyl methacrylate and 44% of α -methylstyrene,

were used, and a mixture containing 61% of methyl methacrylate and corresponding to 65 42% of the total amount of monomer was used in the first step.

Two percent aqueous solution of sulphuric acid was added to the resultant latex to coagulate the polymer, and the coagulated polymer was separated, washed with water, dehydrated, and dried, and thereafter a stabilizer was mixed along with the coagulated polymer. The mixture was made into pellets by using an extruder, and a round disc whose diameter and thickness were respectively 4 inches and $\frac{1}{8}$ inch, and a bar ($\frac{1}{2} \times \frac{1}{2} \times 5$ inches) were shaped by using an in-line screw type 3.5 oz. injection-moulder and the physical properties of the shaped articles were evaluated.

The results obtained are shown in the table along with the results of the following reference examples.

Reference Example 1:

The operation was carried out exactly in the same manner as in Example 1 except that styrene was used in place of methyl methacrylate, and the graft copolymer was obtained at the conversion of 95%.

Reference Example 2:

The operation was carried out exactly in the same manner as in Example 1 except that the amount of methyl methacrylate was adjusted to be 13% based on the total amount of monomers, i.e., 11.2 parts of methyl methacrylate was used in the first step, and 47.8 parts of α -methylstyrene was used in the second step, and the graft copolymer was obtained at the conversion of 95%.

Reference Example 3:

The operation was carried out exactly in the same manner as in Example 1 except that the amount of methyl methacrylate was adjusted to be 47% based on the total amount of monomer, i.e., 39.9 parts methyl methacrylate was used in the first step, and 19.1 parts of α -methylstyrene was used in the second step, and the graft copolymer was obtained at a conversion of 96%.

Reference Example 4:

The operation was carried out exactly in the same manner as in Example 1 except that the amount of α -methylstyrene was adjusted to be 18% based on the total amount of monomer, i.e. 43.7 parts of methyl methacrylate was used in the first step, and 15.3 parts of α -methylstyrene was used in the second step, and the graft copolymer was obtained at a conversion of 95%.

Reference Example 5:

The operation was carried out exactly in the same manner as in the Example 1 except

- that the amount of α -methylstyrene was adjusted to be 67% based on the total amount of monomer, i.e. 2.1 parts of methyl methacrylate was used in the first step, and 56.9 parts of α -methylstyrene was used in the second step, and the graft copolymer was obtained at a conversion of 96%.

Reference Example 6:

- The operation was carried out exactly in the same manner as in Example 1 except for that the amount of the monomer mixture of the first step was adjusted to be 23% based on the total amount of monomer, and 12 parts of methyl methacrylate, 6.0 parts of styrene, and 1.6 parts of acrylonitrile were used in the first step, and 10 parts of methyl methacrylate, 37 parts of α -methylstyrene, 5 parts of styrene, 13.4 parts of acrylonitrile were used in the second step, and the graft copolymer was obtained at a conversion of 95%.

Reference Example 7:

- The operation was carried out exactly in the same manner as in Example 1 except that the amount of the monomer was adjusted to be 52% based on the total amount of monomer in the first step, and 22 parts of methyl methacrylate, 11 parts of styrene, 5.0 parts of acrylonitrile, and 6.2 parts of α -methylstyrene were used in the first step, and 30.8 parts of α -methylstyrene and 10 parts of acrylonitrile were used in the second step, and the graft copolymer was obtained at a conversion of 95%.

Reference Example 8:

- The operation was carried out exactly in the same manner as in Example 1 except for that the amount of methyl methacrylate was adjusted to be 38% based on the monomer used in the first step, i.e. 13.7 parts of methyl methacrylate and 19.3 parts of styrene were used in the first step, and the graft copolymer was obtained at a conversion of 95%.

Reference Example 9:

- The operation was carried out exactly in the same manner as in Example 1 except that the amount of methyl methacrylate was adjusted to be 82% based on the amount of the monomer to be used in the first step, i.e. 29.5 parts of methyl methacrylate and 3.5 parts of styrene were used in the first step, and the graft copolymer was obtained at a conversion of 95%.

Reference Example 10:

- The operation was carried out exactly in the same manner as in Example 1 except that 0.2 part of potassium persulphate was used in place of the sugar containing pyrophosphate formulation as the initiator of the first step, and the same amount of the sugar containing pyrophosphate formulation as in the first step of Example 1, was used in place of potassium persulphate, in the second step, and the conversion was 95%.

TABLE

	(1) Flow rate ($\times 10^{-3}$ cm ³ /sec)	Izod impact strength (kg. cm/ cm ²) (with notch)	Rockwell hardness (R-scale)	(2) Heat dis- tortion tempera- ture (°C)	(3) Heat shrinkage (%)	(4) Surface gloss(%)
ASTM	—	D 256	D 785	D 648		D 673
Example 1	43	20.6	104	96	2.3	76
Reference Example 1	10	18.0	105	90	23.5	75
„ 2	23.4	19.6	104	96	12.4	74
„ 3	30	19.4	104	88	17.4	73
„ 4	39.4	20.3	104	87	18.3	74
„ 5	9.3	17.8	107	96	9.1	65
„ 6	25.4	18.0	104	91	18.3	69
„ 7	58	19.4	103	93	30.2	75
„ 8	44.5	19.2	104	90	19.3	74
„ 9	43	18.5	104	92	11.2	73
„ 10	42	19.6	104	95	4.8	40

Remarks:

(1) Flow rate:

The volume of resin flowing out through a nozzle having a diameter of 1 mm, the length thereof being 2 mm, for one second at 240°C under a load of 30 kg. by means of Koka-type Flow Tester:

(2) Heat distortion temperature:

$\frac{1}{8}$ " \times $\frac{1}{4}$ " \times 5" bar, load 264 psi, without annealing.

(3) Heat Shrinkage:

The degree of shrinkage in a direction of flow caused when a disc, the diameter thereof being 4", the thickness thereof being $\frac{1}{8}$ ", is left out in a Greer's oven at 120°C for one hour.

(4) Surface gloss:

Surface gloss is shown by the percentage of the reflected light to the incident light at an angle of 45° by means of MURAKAMI type glossmeter. When the obtained value is higher than 50%, a gloss can be recognised by the eyes.

5 The above table shows that the heat resistant resin obtained by the present invention possesses low heat shrinkage, excellent processability, high mechanical strength, and excellent surface gloss.

EXAMPLE 2

10 The reaction was carried out in such a manner that 15 parts of polybutadiene latex (as solids) was mixed with 11 parts of styrene, 27 parts of methyl methacrylate, 0.1 part of tertiary dodecyl mercaptan, 1.0 part of dis-

proportionated potassium rosinate, and 150 parts of water, the initiator composed of 0.42 15 part of cumene hydroperoxide, 0.7 part of dextrose, 0.5 part of sodium pyrophosphate and 0.01 part of ferrous sulphate, was added to the reaction mixture with stirring and the reaction was carried out at 70°C for four 20 hours.

The conversion was 94%, and then 37 parts of α -methylstyrene, 10 parts of acrylonitrile, 0.2 part of tertiary dodecyl mercaptan, 1.0 25 part of disproportionated potassium rosinate

and 0.2 part of potassium persulphate were added to the reaction system of the first step, and the reaction mixture was stirred at 60°C for 6 hours, and the conversion was 94%. The quantitative relation between the polybutadiene and vinyl monomers in said graft copolymerization was as follows: 15 parts of polybutadiene and 85 parts of vinyl monomer containing 32% of methyl methacrylate and 44% of α -methylstyrene, were used, and in the first step of polymerization, 45% of the vinyl monomer based on the total amount of monomer was used.

The resulting resin presented a flow rate of 40×10^{-3} cm³/sec., an impact strength of 15.1 Kg.cm/cm², a heat distortion temperature of 96°C, a thermal shrinkage of 0.7%.

EXAMPLE 3

15 parts of polybutadiene latex (as solids) was mixed with the same amount of sugar containing pyrophosphate formulation used as initiator in the first step of the Example 1 with stirring at 70°C, and then an emulsified monomer mixture composed of 11 parts of styrene, 22 parts of methyl methacrylate, 3 parts of acrylonitrile, 0.05 part of tertiary dodecyl mercaptan, 1.0 part of disproportionated potassium rosinate, and 150 parts of water, was continuously added dropwise thereto for two hours and 30 minutes to effect the reaction.

The conversion was 95%. Then the reaction temperature of the first step was lowered to 60°C and 0.2 part of potassium persulphate was added thereto and, while stirring the reaction mixture, an emulsified monomer mixture composed of 37 parts of α -methylstyrene, 12 parts of acrylonitrile, 0.1 part of tertiary dodecyl mercaptan, 1.0 part of disproportionated potassium rosinate, and 100 parts of water was continuously added dropwise for four hours, and then ageing was carried out for two hours.

The graft copolymer was obtained at the conversion of 94%. (The quantitative relation of polybutadiene and vinyl monomers in said graft copolymerization was the same as in Example 1).

The resulting resin presented a flow rate of 64×10^{-3} cm³/sec., an impact strength of 10.5 kg-cm/cm², a heat distortion temperature of 95°C., and a thermal shrinkage of 1.8%.

WHAT WE CLAIM IS:—

1. A method of producing a heat resistant graft copolymer of improved processability which comprises graft copolymerizing from 70 to 95 parts by weight of a vinyl monomer mixture containing 15 to 45% by weight of methyl methacrylate and 20 to 65% by weight of α -methylstyrene with 5 to 30 parts by weight of a synthetic rubber in latex state wherein from 25 to 50% by weight (based on the total amount of vinyl monomer mixture) of the vinyl monomer mixture, containing from 40 to 80% by weight of methyl methacrylate and from 0 to 15% by weight of α -methylstyrene, is graft copolymerized in the presence of an oil soluble organic peroxide initiator, and then the remaining vinyl monomer mixture is graft copolymerized in the presence of a water soluble persulphate initiator.

2. A method as claimed in claim 1 in which the synthetic rubber is a butadiene polymer.

3. A method as claimed in claim 2 in which the butadiene polymer comprises polybutadiene, styrene-butadiene rubber or acrylonitrile-butadiene rubber.

4. A method as claimed in any preceding claim in which the vinyl monomer mixture comprises one of the following combinations:—

methyl methacrylate: α -methylstyrene:styrene, methyl methacrylate: α -methylstyrene:acrylonitrile, and

methyl methacrylate: α -methylstyrene:styrene:acrylonitrile.

5. A method as claimed in any preceding claim in which the organic initiator comprises one or more of benzoyl peroxide, cumene hydroperoxide, diisopropyl-benzene hydroperoxide, and paramenthane hydroperoxide.

6. A method as claimed in any preceding claim in which the persulphate initiator comprises potassium persulphate and/or ammonium persulphate.

7. A method as claimed in claim 1 substantially as described herein with reference to Example 1 or Example 2 or Example 3.

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